PATENT SPECIFICATION

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COMPLETE SPECIFICATION

The Production of Cyano Benzylamines

We, THE DISTILLERS COMPANY LIMITED, a British company, of 12, Torphichen Street, Edinburgh 3, Scotland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the production of aromatic amines, and in particular to the production of aromatic cyano-amines by the selective hydrogenation of aromatic dinitriles.

The catalytic hydrogenation of aromatic nitriles to primary amines has already been proposed. Hitherto, the use of dinitriles as starting materials has normally resulted in the production of diamines.

It is an object of the present invention to provide a process for the hydrogenation of phthalonitrile, isophthalonitrile and terephthalonitrile in which only one of the two cyano groups is selectively hydrogenated, to produce primary and/ or secondary cyano-benzylamines.

According to the present invention the process for the production of cyano-benzylamines comprises hydrogenating phthalonitrile, isophthalonitrile, and/or terephthalonitrile in the liquid phase in the presence of a palladium or platinum catalyst.

It has been found surprisingly that when the hydrogenation of these dinitriles is carried out in the presnce of a palladium or platinum catalyst selective hydrogenation of only one of the two nitrile groups can be obtained. Particularly suitable catalysts for the reaction are palladium and platinum deposited on to a support, such as alumina or carbon. A preferred catalyst is made by depositing 0.1 to 5 parts of palladium onto 99.9—95 parts of powdered alumina. A moderately wide range of catalyst concentrations may be used in the reaction but it is preferred to use low concentrations of catalyst, for instance between 0.005 and 5% by weight based on the weight of the dinitrile solution.

The hydrogenation is suitably carried out in the presence of a solvent or partial solvent for the dinitrile. Suitable conventional hydrogenation solvents which may be used include ammonia and aromatic hydrocarbons such as toluene, and isopropylbenzene, diluted if desired with a polar solvent such as ethanol. If it is desired to produce mainly primary cyano-amines to the substantial exclusion of secondary cyano-amines it is preferred to carry out the hydrogenation in the presence of ammonia, either alone or in admixture with another solvent such as toluene. The amount of ammonia present is not critical, amounts up to twenty times the weight of the dinitrile being suitable. In one method of carrying out the process of this embodiment, a mixture of hydrogen and ammonia vapour is continuously passed through the reaction mixture containing a solvent, such as toluene, which is thereby maintained saturated with ammonia while the hydrogenation is taking place.

The reaction may be carried out over a moderately wide range of temperatures for instance between 0° and 150° C. and over a wide range of pressures. The optimum temperature will vary for different reaction conditions, and factors such as the pressure employed, and the presence or absence of low-boiling solvents such as ethanol or ammonia have to be taken into account. In general, at atmospheric pressure and in the presence of solvents such as ethanol/ammonia a suitable temperature range is from 40—60° C., while at 100 atmospheres pressure a suitable temperature range is 90—100° C. At temperatures of up to about 60° C. the hydrogenation of the second nitrile radical proceeds so slowly that it can in effect be ignored. In this case the reaction can be allowed to proceed until hydrogen uptake substantially ceases, when the mono-amine will have been formed almost exclusively. At temperatures above about 60° C. however, particularly when the starting material is isophthalonitrile, a slow but marked hydrogenation of the second nitrile radical

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may take place after the rapid hydrogenation of the first nitrile radical has been completed. This is evidenced by a continuing slow uptake of hydrogen after the initial rapid uptake has ceased. It may therefore be necessary when operating at high temperatures, to stop the reaction at this point in order to obtain selectively high yields of the mono-amine. Where the reaction is carried out at atmospheric pressure it is preferred to add the dinitrile to the reaction mixture continuously as the reaction proceeds owing to the low solubility of the dinitrile; the reaction products are relatively extremely soluble.

The reaction mixture may be treated for the recovery of the cyano-benzylamine by conventional methods, for instance by distillation to remove ammonia and solvents present, followed by vacuum distillation of the residue. Alternatively the residue may be contacted with water in the presence of which the cyanobenzyl amines have been discovered to form low-melting solid hydrates. By dissolving the residue in water at a temperature above the m.p. of the hydrates any unreacted dinitrile will remain undissolved and can be filtered off. On cooling the cyanobenzylamine hydrate solidifies and can be filtered. However, it is preferred to carry out the reaction so that substantially no dinitrile remains, it being a remarkable feature of the process that this can be effected without the formation of more than minor amounts of diamines, secondary amines, and Schiff's bases. The cyanobenzyl amine can then be recovered from the product by simple distillation.

The following examples are given further to illustrate the process of the present invention. In the examples the parts by weight and parts by volume bear the same relation to each other as do kilograms to litres:—

EXAMPLE 1

A hydrogenation apparatus consisted of a heated reactor fitted with means for agitation and a sump at the bottom, covered with sintered glass, through which hydrogen could be admitted in the form of fine bubbles. The hydrogen was continuously recycled through the apparatus by means of a gas recycling pump, and was mixed with 30—50% of its volume of ammonia by being passed up a packed column countercurrently to a flow of aqueous ammonia and dried by passage over solid caustic soda.

As hydrogen was consumed in the reaction fresh hydrogen was admitted to the system.

The reactor was charged with 1500 parts by volume of a solvent comprising a mixture of sulphur-free isopropyl-benzene and ethyl alcohol in equal amounts, together with 10 parts by weight of powdered alumina, impregnated with 5% of its weight of palladium. The reactor system was then purged thoroughly with the hydrogen/ammonia mixture, and this mixture was recycled through it until the solvent heated to 50° C., was saturated with ammonia.

A charge of 15 parts by weight of terephthalonitrile was introduced into the reactor. Further additions of approximately 15 parts by weight of terephthalonitrile were made as each previous charge became hydrogenated, as indicated by uptake of hydrogen, and passed into solution (the terephthalonitrile did not dissolve completely in the solvent, but the hydrogenated products did). In this manner 100 parts by weight of terephthalonitrile were charged, and the hydrogenation was continued for 19 hours until substantially no more hydrogen was taken up. At this stage 35500 parts by volume of hydrogen had been absorbed, the equivalent of approximately 2.03 moles of hydrogen per mole of terephthalonitrile.

The solvent was removed by flash distillation, and the residual liquid was distilled *in vacuo* with nitrogen cover, to give 100 parts by weight of 4-cyanobenzylamine, a yield of 97%.

The 4-cyanobenzylamine had an equivalent weight as an amine of 130 (theoretical × 132) and was a solid of boiling point 126° C./2 mm., n_D^{20} 1.567, melting point 19° C. The 4-cyanobenzylamine readily formed a hydrate of melting point 45° to 48° C. with water, and with perchloric acid it yielded a perchlorate of melting point 206—209° C.

EXAMPLE 2

The process of Example 1 was repeated except that after saturating the reaction solution with ammonia, no further ammonia was mixed with the recycling hydrogen.

The product after removing the solvent comprised 55% 4-cyano-benzylamine and 45% of a high boiling residue from which an appreciable amount of bis(4-cyanobenzyl)-amine, m.p. 104° C. a secondary amine derived from 4-cyano-benzylamine, was isolated. It yielded a perchlorate of m.p. 268—270° (with decomposition).

EXAMPLE 3

The process of Example 1 was repeated except that the starting material was isophthalonitrile. The isophthalonitrile was fed to the apparatus in batches of about 20 parts by weight, the total amount introduced being 150 parts by weight in 17 hours.

The amount of hydrogen absorbed was 107% of the theoretical requirement of 3-cyanobenzylamine, and the end of the reaction was marked by a considerable slowing down of the absorption rather than by an almost complete cessation.

After removing the solvents and distilling the product, 143 parts by weight of an oil was obtained, having a boiling point of 115° C./1 mm. The equivalent weight of the product as an amine was 145 (corresponding to 91% 3-cyano-benzylamine) and representing a yield of 85% on the isophthalonitrile taken. The higher boiling residue, containing second-

ary amines, amounted to only 9 parts by weight.

The 3-cyanobenzylamine was an oil n_D^{20} 1.563 which yielded a hydrate of melting point 25° C., with water.

EXAMPLE 4

1 part by weight of terephthalonitrile, 12.2 parts by weight of liquid ammonia and 0.014 parts by weight of palladium deposited on 0.27 parts of alumina were contacted with excess of hydrogen at 90—100° C./90—105 atmospheres pressure for 0.75 hours, when reaction ceased. The reaction was followed by the uptake of hydrogen. On releasing the pressure the ammonia distilled off, and the residue consisting of mono-nitrile and unreacted dinitrile was distilled to recover 4-cyano-benzylamine in about 50% yield. About 0.4 parts of terephthalonitrile were also recovered unchanged.

EXAMPLE 5

1 part by weight of isophthalonitrile, 2.4 parts by weight of liquid ammonia, 6.9 parts by weight of toluene, and 0.04 parts by weight of Adams' catalyst (platinum oxide) were contacted with excess of hydrogen at 95—105° C. /100—150 atmospheres pressure for 1.3 hours and when absorption of hydrogen ceased, 3-cyano-benzylamine was isolated from the residue in about 60% yield.

The cyanobenzylamines produced by the process of the present invention are useful intermediates in the production of the corresponding benzylamine carboxylic acids which are starting materials for the preparation of polyamide fibres.

WHAT WE CLAIM IS:—

1. The process for the production of cyanobenzylamines which comprises hydrogenating phthalonitrile, isophthalonitrile, and/or terephthalonitrile in the liquid phase in the presence of a palladium or platinum catalyst.

2. The process as claimed in Claim 1 wherein the catalyst is deposited on a support.

3. The process as claimed in Claim 2, wherein the support is alumina or carbon.

4. The process as claimed in Claim 1, wherein the catalyst consists of 0.1 to 5 parts of palladium deposited on 99.9 to 95 parts of powdered alumina.

5. The process as claimed in any of the preceding claims wherein the concentration of catalyst is between 0.005 and 5% by weight of metal based on the weight of the dinitrile starting material.

6. The process as claimed in any of the preceding claims wherein the hydrogenation is carried out in the presence of a solvent or partial solvent for the dinitrile.

7. The process as claimed in Claim 6 wherein the solvent is an aromatic hydrocarbon.

8. The process as claimed in Claim 7 wherein the solvent is toluene.

9. The process as claimed in Claim 7 wherein the aromatic hydrocarbon is diluted with a polar solvent such as ethanol.

10. The process as claimed in Claim 6 wherein the solvent is ammonia.

11. The process as claimed in Claim 10 wherein the ammonia is mixed with an aromatic hydrocarbon.

12. The process as claimed in Claims 10 or 11 wherein the hydrogenation is carried out in the presence of up to 20 parts by weight of ammonia based on the weight of the dinitrile.

13. The process as claimed in any of the preceding claims wherein the hydrogenation is carried out at a temperature between 0 and 150° C.

14. The process as claimed in Claim 13 wherein the hydrogenation is carried out at a temperature between 40 and 60° C. and at atmospheric pressure.

15. The process as claimed in Claim 13 wherein the hydrogenation is carried out at a temperature between 90 and 100° C. and at 100 atmospheres pressure.

16. The process for the production of cyanobenzylamines substantially as described in the examples.

17. Cyano-benzylamines when produced by the process of any of the preceding claims.

N. F. BAKER,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

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It is an object of the present invention to provide a process for the hydrogenation of phthalonitrile, isophthalonitrile and terephthalonitrile in which only one of the two cyano groups is selectively hydrogenated, to produce primary and/or secondary cyano-benzylamines.

According to the present invention the process for the production of cyano-benzylamine comprises hydrogenating phthalonitrile, iso-

phthtalonitrile, and/or terephthalonitrile in the liquid phase in the presence of a noble metal catalyst.

It has been found surprisingly that when the hydrogenation of these dinitriles is carried out in the presence of a noble metal catalyst selective hydrogenation of only one of the two nitrile groups can be obtained. Particularly suitable catalysts for the reaction are palladium and platinum, preferably deposited onto a support, such as alumina or carbon. A preferred catalyst is made by depositing 1 to 5 parts of palladium onto 99—95 parts of powdered alumina. A moderately wide range of catalyst concentrations may be used in the reaction but it is preferred to use low concentrations of catalyst, for instance between 0.1% and 5% by weight based on the weight of the dinitrile starting material.

The hydrogenation is suitably carried out in the presence of a solvent or partial solvent for the dinitrile. Suitable conventional hydrogenation solvents which may be used include aromatic hydrocarbons such as toluene, diluted if desired with a polar solvent such as ethanol. If it is desired to produce mainly primary cyano-amines to the substantial exclusion of secondary cyano-amines it is preferred to carry out the hydrogenation in the presence of ammonia, either alone or in admixture with another solvent such as toluene. The amount of ammonia present is not critical, amounts up to twenty times the weight of the dinitrile being suitable; however, to suppress the formation of secondary amines, it is preferred to use at least two parts of ammonia to one part of dinitrile. In one method of carrying out the process of this embodiment, a mixture of hydrogen and ammonia vapour is continuously passed through the reaction mixture containing a solvent, such as toluene, which is thereby maintained saturated with ammonia while the hydrogenation is taking place.

The reaction may be carried out over a moderately wide range of temperatures for instance between 0° and 150° C. and over a wide range of pressures. The optimum temperature will vary for different reaction conditions, and factors such as the pressure employed, and the presence or absence of low-boiling solvents such as ethanol or ammonia have to be taken into account. In general, at atmospheric pressure and in the presence of solvents such as ethanol/ammonia a suitable temperature range is from 40—60° C., while at 100 atmospheres pressure a suitable temperature range is 90—100° C. At temperatures of up to about 60° C. the hydrogenation of the second nitrile radical proceeds so slowly that it can in effect be ignored. In this case the reaction can be allowed to proceed until hydrogen uptake substantially ceases, when mono-amine will have been formed almost exclusively. At temperatures above about 60° C. however, particularly when the starting material is isophthalonitrile, a slow but marked hydrogenation of the second nitrile radical may take place after the rapid hydrogenation of the first nitrile radical has been completed. This is evidenced by a continuing slow uptake of hydrogen after the initial rapid uptake has ceased. It may therefore be necessary when operating at high temperatures, to stop the reaction at this point in order to obtain selectively high yields of the mono-amine. Where the reaction is carried out at atmospheric pressure it is preferred to add the dinitrile to the reaction mixture continuously as the reaction proceeds owing to the low solubility of the dinitrile; the reaction products are relativly extremely soluble.

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